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SYNTHESIS AND CHARACTERIZATION OF BLOCK COPOLYMERS(U)
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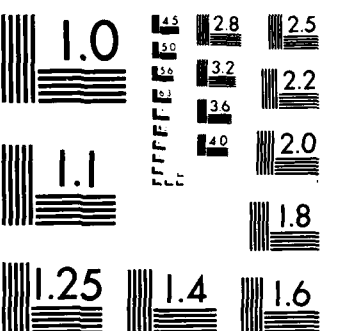
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SYNTHESIS AND CHARACTERIZATION OF BLOCK COPOLYMERS

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SYNTHESIS AND CHARACTERIZATION OF BLOCK COPOLYMERS

by Jin-Long Hong

1. Segmented (AB)_n¹ Polyurethanes;

A series of polyether-polyurethane (PEPU) segmented block copolymers were synthesized and characterized. Soft segments were poly(propylene oxide) (PPO; $\bar{M}_n^1 = 2,000$) or poly(tetrahydrofuran) (PTHF; $\bar{M}_n^1 = 1,650$). Hard segments were formed from 4,4'-diphenylmethane diisocyanate (MDI) and different short chain diols as chain extenders. In the PPO series 1,5-pentandiol (P), diethylene glycol (D), triethylene glycol (T) and 1,3-bis(N,N'-methyl-N,N'-2-hydroxyethyl)isophthalamide (Bi(M)) were used as chain extenders. In the PTHF series 1,6-bis(N,N'-2-hydroxyethyl)adipamide (A), Bi(M), D, T, bis(N,N'-2-hydroxyethyl)isophthalamide (Bi) and 1,6-bis(N,N'-methyl-N,N'-2-hydroxyethyl)adipamide (A(M)) were used as chain extenders. By varying hard segment content, PEPU polymers with different properties were synthesized. ←

Degree of phase separation was investigated by IR and low temperature DSC. IR revealed the relative degree of phase separation or hard segment crystallinity of PEPU copolymers. Low temperature DSC showed the relationship between glass transition temperature of soft segment and hard segment content, which gave direct information about degree of phase separation in each polymers. In the PPO-based series, P- and D-extended PEPU polymers have higher degrees of phase separation than Bi(M)- and T-extended PEPU polymers. In the PTHF-based series, the relative

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degree of phase separation decreases in the following order, A- > D- > Bi(M)- > T-extended polymers. Therefore, degree of phase separation is greatly influenced by the chemical structures of chain extenders. Triethylene glycol (T), with its long chain and high content of flexible ether bonds, should have the highest flexibility of all the chain extenders described above. Diethylene glycol (D), with two flexible C-O linkages in place of the central C-C bonds of pentanediol (P), will be intermediate in flexibility between triethylene glycol and pentanediol. Chain extenders with a higher degree of flexibility will decrease the crystallinity in the hard domain and also increase the hard-soft phase mixing. Therefore, PPO-based PEPUs extended from triethylene glycol are viscous liquids to gummy materials. This suggests the absence of hard domain structure. In addition to flexibility, chain extenders with higher density of polar groups and hydrogen bonding capability (such as Bi and A) should elevate the crystallinity of hard domain and the degree of phase separation. However, the presence of N-methyl groups and benzene rings in chain extenders (such as Bi(M)) sterically inhibits formation of well-packed crystalline hard domains.

These factors such as degree of phase separation, crystallilnity in the hard domain and chemical structure of soft segment all contribute to polymers' mechanical properties. Generally, a higher degree of phase separation resulted in higher values of Young's modulus and stress at break. This is especially true for PTHF-based copolymers. Thermal transitions of above polymers were detected from DSC and DMTA measurements.

PPO-based polymers possess T_{sg} , T_{hg} and T_m which correspond to glass transitions of soft, hard segment and melting of hard crystalline domain respectively. In the PTHF series, polymers possess crystallization and melting transitions of the soft segment in addition to those transitions observed in the PPO series. In either PPO- or PTHF-based series, melting of hard crystalline domains was accompanied by decomposition.

2. Styrene-THF-Styrene Triblock Copolymer

A-B-A triblock copolymer with A block as polystyrene and B block as poly(tetrahydrofuran) (PTHF) was synthesized by coupling a slight excess of monohydroxyl-terminated polystyrene (PS-OH) with isocyanate-terminated PTHF prepolymer, $OCN-(PTHF)_n-NCO$. Therefore, urethane groups served as linkage between A and B blocks.

IR, GPC and simple visual observation demonstrated the effectiveness of this coupling process. Solvent-cast films were clear and tough and 1H -NMR analysis revealed a styrene content of 50% by weight. DSC analysis showed a high degree of phase separation for this copolymer. Also, this triblock copolymer did not flow below $125^\circ C$, a temperature much higher than glass transition temperature of styrene block.

3. Acid-Catalyzed Decomposition of Polyether, Polyacetal and Urethane Copolymers

PTHF and poly(1,3-dioxepane) (PDXP) in addition to their acetate- and phenyl isocyanate-end capped derivatives as well as

PTHF-based PEPUs synthesized from A, Bi(M), D and T were the subjects of TGA studies of thermal and acid-catalyzed decomposition studies. Ethyl 2-naphthalenesulfonate (ET-NS) was used as acid-generator to catalyze polymer decomposition.

Homopolymers PTHF, PDXP, acetate-capped PTHF and PDXP showed enhanced decomposition in the presence of ET-NS as compared with thermal decomposition. Acetate end-capping improved thermal stability to thermal and acid-catalyzed decomposition.

PEPUs synthesized from amide type chain-extendors such as A and Bi(M) exhibited no acid-catalyzed decomposition. This contrasts with PEPUs copolymers synthesized from D and T chain-extendors, in which acid-catalyzed decomposition was observed. The possible role of amide linkages in PEPUs as acid neutralizer (base) is proposed.

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